TRACE ELEMENT DISTRIBUTIONS IN COAL GASIFICATION PRODUCTS

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INTRODUCTION

The determination of the fate and distribution of trace elements during coal conversion is an important and prerequisite task if such an industry is to be implemented on a massive scale. Considering the overwhelming abundance of native coal resources, an implementation of this magnitude is a distinct possibility in the near future. Coal gasification is currently under investigation by many organizations in the U.S. as an alternative source of environmentally acceptable fuels. In conjunction with ongoing coal gasification studies at this laboratory, trace element investigations have been performed to help assess potential environmental impacts of coal gasification processes. This work presents preliminary findings of trace and minor element distributions in the process streams of the SYNTHANE Gasifier Process Development Unit located at this laboratory.

EXPERIMENTAL

Three separate gasification runs were made with the SYNTHANE Gasifier PDU using Montana sub-bituminous 'C' coal. The SYNTHANE Gasifier characteristics and operating conditions have been described previously (1-3). Maximum average temperatures attained in this unit are typically 950-1000°C. A schematic diagram of the PDU is presented in Figure 1.

An integral part of this study was the sampling of the process streams of the gasification unit. Samples collected for subsequent analysis included the feed coal and feed water (major input streams) and gasifier char, filter fines, and condensable water and tars (major output streams). Sampling points in the PDU are illustrated in Figure 1. The feed coal was systematically thieved during the loading of the gasifier hopper in order to obtain representative samples of this process stream. Feed water (for generation of process steam) was also periodically sampled during the gasification runs. The gasifier char, condensable tars and water, and particulate matter from the gas product stream were collected after each run. The weights of the process streams sampled are reported in Table 1. Also shown are the weight percentages that the samples represent relative to the total amount of the process stream consumed or produced. In most cases, the entire process stream was collected. This procedure ensured representative sampling of these process streams.

Considerable efforts were required to homogenize these samples. The solid process streams were riffled, ground and further comminuted to manageable sizes. In some cases, further grinding to -325 mesh was required. Condensate water analytical samples were taken while vigorously stirring the bulk sample. The con-

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densate tar process stream presented unique sampling problems. This process stream consists of organic and aqueous phases, in addition to a considerable amount of solid material. Due to the immiscibility of these phases, it was not possible to withdraw homogenous samples by merely mixing the process stream. This problem was overcome by adding tetrahydrofuran to the sample to render the various phases miscible.

Samples were analyzed by spark-source mass spectrometrometry (SSMS) and atomic absorption spectrophotometry (AAS). Approximately 65 elements were semi-quantitatively determined in each process stream by SSMS 'survey' analyses. The feed coal, char, and filtered particular matter process streams were low-temperature ashed, mixed with high purity graphite, and formed into electrodes. Unashed samples were also analyzed for the determination of volatile elements. Aqueous and wet-ashed samples were mixed with graphite and gently dried under an infrared lamp. Photoplate detection was utilized with computer assisted quantitation by means of the Hull equation (4). Figure 2 illustrates a typical SSMS 'survey' analysis of the feed coal process stream. Such analyses are generally accurate to within a factor of three and are especially valuable for the complete inorganic characterization of these process streams.

Isotope dilution spark-source mass spectrometric (ID-SSMS) determinations were also performed. Samples were solubilized by means of Parr acid digestion bombs (5-7) after addition of enriched isotopes. Elements of high environmental interest (Ni, Cu, Se, Cd, Pb, and Tl) were preconcentrated by means of electrodeposition onto high-purity gold electrodes. These electrodes were then sparked in the spectrometer. Quantitation was accomplished using the isotope dilution equation of Paulsen (8-10). Results of ID-SSMS measurements on the three solid process streams are presented in Table 2. Quadruplicate analyses were made, with the precision of such measurements ranging from 2-15% (relative standard deviation).

Atomic absorption determinations of seven elements (Mn, Ni, Cu, Cr, As, Pb, and Cd) were also made. Samples were solubilized by means of high temperature ashing and lithium metaborate fusion for the determination of Mn, Ni, Cu, and Cr (11). Digested sample solutions were aspirated into the atomic absorption spectrometer and quantitated by the method of standard additions. Pb and Cd were preconcentrated by extracting their iodide complexes into methyl isobutyl ketone (MIBK) prior to aspiration into the spectrometer. Arsenic was determined using hydride evolution AAS after wet-ashing of the samples. Results of the AAS determinations of the solid process streams are shown in Table 3. The precision of these determinations ranged from 2-20% r.s.d.

DISCUSSION

All process streams were surveyed for approximately 65 elements by conventional SSMS analyses. Such analyses, although semi-quantitative, provide quick multi-element analyses that are valuable when the inorganic composition of the process streams are unknown and/or unsuspected. This type of analysis is especially useful for process monitoring applications, resulting in an almost complete inorganic characterization of process streams from such a conversion unit. This kind of characterization is especially useful in delineating potential problems and pointing out the need for more accurate analyses of specific elements. As an example of the kind of information that can be extracted from such data, an enrichment ratio can be calculated for various elements based on their concentrations in the filter fines process stream relative to their concentrations in the feed coal (after correcting for the varying ash contents in the two process streams). Table 4 presents the enrichment ratios for a number of elements. An enrichment ratio of unity indicates no enrichment, while ratios greater than unity indicate enrichment in the filter fines process stream. If an enrichment ratio of three or greater is assumed to be significant (to take into account the uncertainty limitations of the technique), then elements can be classified as either enriched or not enriched. Table 4 shows that many elements are shown to be enriched to a great degree. Presumably, such enrichment is due to a volatilization of these elements in the

high temperature zone of the reactor and subsequent condensation of these volatilized elements in the cooler sections of the gasification unit. Although such a mechanism has been shown to be operative in high temperature coal combustion (12-13), this may be the first work showing such a mechanism to be operative during coal gasification. Preliminary SSMS analyses of size-separated filter fines fractions substantiates this finding.

Both the SSMS survey results and the more accurate, precise results obtained by ID-SSMS and AAS show the gasifier char to be the major elemental 'sink' for most elements. This has important environmental ramifications in that this material may be utilized as a combustion material for production of process steam. The fate of the environmentally important elements during this combustion will need to be determined. On the other hand, if the char is disposed of as an alternative to its by-product utilization, significant solid waste problems will almost certainly occur.

Selenium, as determined by ID-SSMS, showed a distribution among the process streams that was markedly different from the bulk of the other elements studied. The major elemental sink for Se was the condensate water process stream. Significant quantities of this element were also found in the condensate tar. This finding can be rationalized in terms of the high volatility of this element. Arsenic, as determined by AAS, does not exhibit such behavior, in contrast to what one might expect for this element. The major sink for this element is the gasifier char. This fact seems to indicate that the arsenic is present in the coal in a non-volatile form and that it is not converted to a volatile form during the gasification process.

Mass balances of elements across a conversion unit may be valuable in predicting the release rates of certain elements to the environment. Such balances can be calculated knowing the concentration of the element in each process stream and the mass of the respective process stream. Mass balances of 100% at the trace level are generally exceedingly difficult to obtain in such complex, open systems as a gasification reactor. Results of such mass balances are shown in Table 5. The data were calculated using the AAS and/or the ID-SSMS concentration values for the elements in the major process streams. The data indicate that the bulk of most elements (Cu, Ni, Mn, Pb, Cr) are being retained within the unit. However, other elements cannot be fully recovered (i.e., Cd and Se) and careful considerations of the fate of these elements must be made in view of their environmental and toxicological hazards.

ACKNOWLEDGMENT

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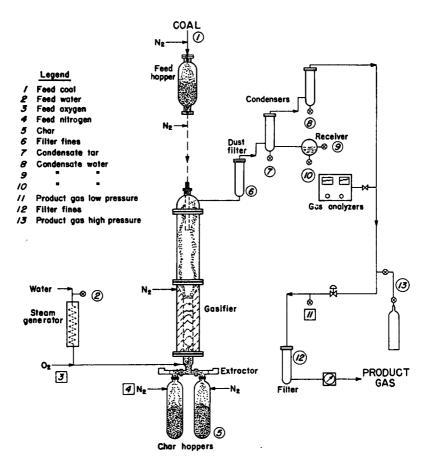
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Table 1

Description of Sample Sizes Taken from SYNTHANE Process Development Unit
for Trace Element Studies

Sample	Run Number		
	293	294	295
Feed Coal, kg	7.7 (11.0)[1]	5.9 (8.0)	6.1 (8.6)
Feed Water, kg	4.9 (5.4)	4.2 (4.8)	4.2 (4.4)
Gasifier Char, kg	17.0 (100)	16.9 (100)	17.0 (100)
Condensate Tar/Water, kg	14.6 (100)	15.5 (100)	15.2 (100)
Condensate Water, kg	52.8 (100)	53.1 (100)	53.5 (100)
Filter Fines, kg	0.4 (100)	0.4 (100)	0.5 (100)
Product Gas, kl	1.7 (1.5)	1.7 (1.4)	1.6 (1.4)

[1]Data in parentheses indicate the percentage of the process stream that was taken for preparation and analysis.

COAL

Legend

1 Feed coal
2 Feed water
3 Feed oxygen
4 Feed nitrogen
5 Char
6 Filter fines
7 Condensate tar
8 Condensate water
9 ▪ ▪
10 ▪ ▪
11 Product gas low pressure
12 Filter fines
13 Product gas high pressure

Figure 1 **Sampling points on the PETC SYNTHANE Process Development Unit.**

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Concentration (ppm, wt)

H --																	
Li 1.8	Be 0.9											B 190	C --	N --	O --	F --	
Na 210	Mg 3100											Al 1.3%	Si 2.1%	P 210	S 1.3%	Cl 35	
K 220	Ca 1.2%	Sc 3.2	Ti 560	V 6.3	Cr 9.6	Mn 700	Fe Ref.	Co 4.9	Ni 4.3	Cu Ref.	Zn 6.3	Ga 3.0	Ge 0.6	As 2.1	Se 2.3	Br 1.5	
Rb 1.8	Sr 270	Y 2.5	Zr 31	Nb 5.9	Mo 1.3	Tc --	Ru ≤1.	Rh <0.2	Pd ≤0.4	Ag ≤0.4	Cd ≤0.7	In ≤0.1	Sn 1.0	Sb 0.7	Te ≤1.	I ≤0.5	
Cs 0.3	Ba 470	La 2.8	Hf 2.3	Ta --	W 2.2	Re ≤0.6	Os --	Ir --	Pt --	Au --	Hg --	Tl ≤0.4	Pb 9.2	Bi 0.4	Po --	At --	
Fr --	Ra --	Ac --	Th 5.5	Po --	U 1.8												

Ce 5.4	Pr 1.7	Nd 6.3	Pm --	Sm 0.8	Eu 0.3	Gd 1.8	Tb 1.3	Dy 1.4	Ho 0.1	Er 0.5	Tm 0.1	Yb 1.0	Lu 0.1

Figure 2 – Elemental survey of Run #293 Feed Coal. Data compiled from low temperature ash, high temperature ash, and whole coal analyses.

Table 2 - Element Concentrations (ppm, wt.) in Gasifier Samples by ID-SSMS Analysis

Sample	Element	Run Number 293	294	295
Feed Coal	Ni	2.83	2.56	2.39
	Cu	7.50	7.52	7.24
	Se	0.56	0.54	0.54
	Cd	0.12	0.12	0.14
	Tl	0.05	0.04	0.04
	Pb	5.14	4.80	4.77
Gasifier Char	Ni	11.6	9.06	11.6
	Cu	25.5	24.2	27.8
	Se	0.14	0.21	0.19
	Cd	0.10	0.12	0.13
	Tl	0.11	0.12	0.15
	Pb	21.2	17.1	19.3
Filter Fines	Ni	10.3	11.5	10.0
	Cu	105	150	131
	Se	0.65	0.94	0.74
	Cd	2.16	2.88	1.81
	Tl	0.09	0.11	0.10
	Pb	13.7	13.5	12.47

Table 3 - Element Concentrations (ppm, wt.) in Gasifier Process Streams by AAS Analysis

Sample	Element	Run Number 293	294	295
Feed Coal	Cr	7.1	6.6	7.9
	Mn	547	512	646
	Ni	2.2	2.7	2.4
	Cu	10.2	9.7	10.4
	As	1.6	1.5	2.0
	Cd	0.07	0.07	0.09
	Pb	5.5	4.6	5.3
Gasifier Char	Cr	32.4	33.5	30.3
	Mn	2510	2350	2430
	Ni	10.8	8.5	8.0
	Cu	33.0	23.8	27.0
	As	6.3	6.0	5.7
	Cd	0.06	0.05	0.05
	Pb	19.6	18.2	18.9
Filter Fines	Cr	12.4	18.5	20.7
	Mn	519	530	503
	Ni	10.0	12.5	10.6
	Cu	114	154	142
	As	9.1	7.9	11.0
	Cd	1.86	2.25	1.75
	Pb	14.1	13.8	15.6

Table 4 - Enrichment Ratios (E_r) for Various Elements

Non-Enriched Elements		Enriched Elements	
Element	E_r	Element	E_r
Na	2.0	K	3.1
Mg	2.7	Rb	6.5
Al	1.0	Co	4.1
Si	1.2	Ni	3.0
Ca	0.8	Zn	7.0
Ti	1.1	Cu	9.3
Zr	2.9	Ga	4.7
Fe	0.8	Ge	11.0
Cr	1.6	As	6.2
Be	2.4	Br	11.0
Sr	1.2	Sn	3.3
Ba	1.1	Sb	5.7
Hf	1.5	I	14.0
Gd	0.8	Mo	7.3
		Pb	3.8
		Cd	6.5

Table 5 - Elemental Mass Balances

	Mass Balance, %		
Element	293	294	295
Cu (ID-SSMS)	103	92	110
Cr (AAS)	112	118	96
Ni (AAS)	122	75	85
Se (ID-SSMS)	45	44	46
Cd (AAS)	36	35	27
Cd (ID-SSMS)	36	46	33
Pb (ID-SSMS)	102	84	101
Pb (AAS)	88	92	89
As (AAS)	99	95	74